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Solid State Spectroscopy Group

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Research Activities

1. OPTICAL PROPERTIES OF MEZOSCOPIC PARTICLES

a. Subpicosecond Spectroscopy of CuCl Nanocrystals II

(S. Yano, A. Yamamoto, K. Edamatsu, A. Kasuya, T. Itoh and T. Goto)

In CuCl nanocrystals, we have observed the change of the exciton absorption spectrum after strong pulsed light irradiation and measured excitation power and size dependences of the absorption change for different radii using subpicosecond pump and probe method at 77K. These experimental results are explained by a cascade model and we discuss about the effect of exciton complex including the biexciton.

b. Excitons in CuBr Microcrystals Embedded in Polymer

(T. Nogami and T. Goto)

We have fabricated CuBr microcrystals embedded in polymethyl methacrylate (PMMA) and measured these absorption and luminescence spectra. In the absorption spectra, the Z_{12} and Z_3 exciton peaks show blue shift by quantum size effect. We have found a new Raman line with the shift of 80 cm^{-1} in the resonance Raman scattering spectra at 2K and a new band at the luminescence energy position of two-LO phonon assisted exciton annihilation.

c. Raman Scattering in PbI_2 Clusters Incorporated into Zeolite Cages

(Z.K. Tang, Y. Nozue and T. Goto)

Raman spectra of PbI_2 clusters in zeolite FAU and LTA are reported. A new Raman band with low frequency in the acoustic phonon region was observed in the cluster. The Raman shift was observed in the cluster. The Raman shift was found to increase in inverse proportion to the radius of the cluster. In the optical phonon region, broad and weak Raman signals were observed, in contrast to the sharp and strong Raman bands in the bulk. The experimental results showed that the electron-acoustic phonon coupling via deformation potential interaction was the main process of the electron-phonon interaction due to the localization of the vibrational motion and the wavefunctions of the carriers in a small cluster, while Frohlich coupling to optical phonons became unimportant because of the neutralization of the electronic charge density. The quantized vibrational eigenmodes were calculated for the cluster. The calculated lowest spherical mode was in good agreement with the observed low-frequency Raman shift.

d. Vibrational Properties and Structure of C_{60} Thin Films on Si(111)7×7 and Graphite Surfaces

(S. Suto, A. Kåsuya, S.W. Hu, A. Wawro, T. Goto and Y. Nishina)

We have investigated vibrational modes of C_{60} thin films adsorbed on the Si(111)7×7 and graphite surfaces using high-resolution electron-energy-loss spectroscopy in combination with scanning tunneling microscopy (STM). The energy-loss spectra are different in energies and in oscillator strengths for the two surfaces. The differences are attributed to the surface morphology observed by STM. The relation between macroscopic dielectric theory manifested by electron-energy-loss and microscopic structure measured by STM is discussed in terms of dielectric function theory.

e. Subpicosecond Spectroscopy of the Optical Nonlinearities of CuCl Quantum Dots

(K. Edamatsu, S. Iwai, T. Itoh, S. Yano and T. Goto)

We have observed ultrafast time-resolved nonlinear optical absorption spectra of confined excitons in CuCl quantum dots embedded in a NaCl matrix. The main part of the nonlinear change consisted of blueshifts of the Z_3 and Z_{12} exciton bands, and their decay had two time constants that coincide with the luminescence lifetimes of excitons and of excitonic molecules. A microscopic mechanism for the optical nonlinearities of confined excitons is discussed.

2. OPTICAL PROPERTIES OF ULTRATHIN CRYSTALS

a. Spatial-Confinement Effect on Phonons and Excitons in PbI_2 Microcrystallites

(S. Saito and T. Goto)

We have measured resonant Raman spectra and exciton absorption spectra of PbI_2 microcrystallites embedded in ethylene metacrylic acid (E-MAA) copolymer at 77 and 2 K, respectively. The microcrystallites are plateletlike and vary in thickness. In the resonant Raman spectra, a new line is observed in the acoustic-phonon energy region, which is intimately related to the exciton absorption band in the ultrathin microcrystallite with finite number of layers. The phonon energy as a function of the crystal thickness is explained on the basis of the finite chain model. From

this analysis, the relationship between the exciton absorption band and the number of layers is confirmed. Using this relation, we reinterpret the dependence of the exciton energy on the layer thickness, which has been measured previously. Consequently, the thickness dependence of the exciton energy is well explained by the quantum confinement model of the exciton translational motion in the crystallites with more than five layers. In crystallites with thinner layers, however, the exciton energies deviate from the theoretical values.

b. The Photoluminescence from ZnS/(ZnSe)n/ZnS Single Quantum Well

(S. Koyama, M.Y. Shen, T. Goto, K. Arai, A. Kasuya and T. Yao)

Using the concept developed in previous researches on temperature dependence of the radiative lifetime of confined exciton in low dimensional system, we have investigated ZnS/(ZnSe)n/ZnS single quantum well system by picosecond optical measurement techniques. It is found that the decay curve of 1 monolayer (ML) ZnSe system is fitted by a stretched exponential and that the radiative lifetime of the confined exciton in 1ML is independent of the temperature below 40K. These phenomena are much different from those of 5ML system. The result for 1ML system shows the property of quantum dot system caused by the lateral quantum confinement effect in 'quantum slabs' of various sizes formed on islands and valleys at the interface.

c. Subpicosecond Spectroscopy of PbI_2 Microcrystallites Embedded in E-MAA Copolymer

(A. Yamamoto, S. Yano, T. Goto and A. Kasuya)

Time-resolved nonlinear optical absorption of PbI_2 microcrystallites embedded in ethylene methacrylic acid (E-MAA) co-polymer was studied by means of the pump-and-probe technique with subpicosecond time resolution. It is found that in 2-4 monolayer (ML) PbI_2 microcrystallites the absorption recovers very fast ($\sim$4ps) and in thicker (more than 9ML) microcrystallites the recovery time increases with the thickness.

d. Diamagnetic Shift of Exciton Level in Ultra-Thin PbI_2 Crystals

(T. Goto, H. Tanaka, M.Y. Shen, S. Sasaki and N. Miura)

Exciton absorption spectra of ultra-thin PbI_2 microcrystallites embedded in organic polymers have been measured under pulsed high magnetic fields up to 150 T at about 10 K. Diamagnetic shifts as well as paramagnetic splittings are observed for σ^+ and σ^- polarizations in the Faraday configuration. From the diamagnetic shifts in the microcrystallites with 3 and 4 layers, the diamagnetic coefficient of both the crystallites is estimated to be 3×10^{-7} Ev/T^2, which is smaller than that estimated with the effective mass approximation. This fact suggests that the exciton wave function shrinks not only via spatial confinement, but via dielectric screening.

3. EXCITON DYNAMICS IN ORGANIC MATERIALS

a. Non-Radiative Relaxation of Photochromic Fulgide

(J. Takeda, S. Kurita, Y. Yokoyama and T. Goto)

The luminescence spectra and the time response of the luminescence of the colored form of furylfulgide dispersed in a polymer film were measured for various concentrations. The infrared spectra of furylfulgide were also measured in order to elucidate the vibrational mode relevant to the

decay of the luminescence. We found that the luminescence spectrum at low concentration consists of at least three luminescence bands and that the decay time of the highest energy luminescence band is three times larger than that of the lowest energy luminescence band. These results are explained in terms of the non-radiative transition model by Gutsche. The frequency of the vibrational mode relevant to the non-radiative decay process and the minimum energy distance between the excited state and the ground state of the colored form of the fulgide are also estimated by the same model.

b. Breakdown of the k Selection Rule and the ^1L_b Exciton Bandwidth in Pyrene Microcrystallites

(Y. Oeda, O. Nishi, Y. Matsushima, K. Mizuno, A.H. Matsui, M. Takeshima and T. Goto)

The ^1L_b exciton bandwidth in pyrene microcrystallites embedded in PMMA films are obtained analyzing excitation spectra at 2K. The bandwidth increases linearly with microcrystallite size and takes its maximum value of 330 cm^{-1}, and then it falls down abruptly to zero. From the observed fact it is suggested that the k selection rule recovers for large microcrystallites.

The lattice relaxation energy and the self trap depth for the V state are obtained to be $\leqq 180 cm^{-1}$ and $\leqq 15\ cm^{-1}$ respectively.

c. Exciton Dynamics and Relaxation Process in Permethylsilane

(H. Suzuki, S. Suto, T. Goto, A. Watanabe and M. Matsuda)

We have measured time response and temperature dependence of photoluminescence in permethylhexasilane film. We propose existence of two types of self-trapped excitons and explain the origin of two decay components.

d. Exciton Dynamics of Poly(methylphenylsilane)

(S. Suto, H. Suzuki, T. Goto, A. Watanabe and M. Matsuda)

We have measured time response of the photoluminescence in σ-conjugated polymer, poly(methylphenylsilane), film at 2K. The site-selective luminescence spectrum and the time response are discussed on the basis of the free and localized states of excitons in disordered system.

4. NON-LINEAR OPTICS OF Cu_2O CRYSTALS

a. Resonant Hyper-Scattering of Orthoexciton in Cu_2O

(M.Y. Shen, S. Koyama, M. Saito, T. Goto and N. Kuroda)

The resonant hyper-scattering of Cu_2O is studied. In the case of polycrystal, the spectral structure of the signal is mainly composed of resonant hyper-Rayleigh and resonant hyper-Raman scattering of Γ_{12}^- phonon. While in the case of single crystal, the second harmonic generation (SHG) as well as the hyper-Rayleigh are obtained. The polarization property of the signal is also obtained. The strong resonant signal can be microscopically understood by the small damping constant of the orthoexciton.

Publications

1) Subpicosecond Spectroscopy of CuCl Nanocrystals II,

S. Yano, A. Yamamoto, K. Edamatsu, A. Kasuya, T. Itoh and T. Goto,
Proc. of the Asia Symposium on Solid State Photophysics, Nara, (1995) 25-28.

2) Excitons in CuBr Microcrystals Embedded in Polymer,
T. Nogami and T. Goto,
Proc. of the Asia Symposium on Solid State Photophysics, Nara, (1995) 319-321.

3) Raman Scattering in PbI_2 Clusters Incorporated into Zeolite Cages,
Z.K. Tang, Y. Nozue and T. Goto,
Materials Science and Engineering B35, (1995) 410-416.

4) Vibrational Properties and Structures of C_{60} Thin Films on Si(111)7×7 and Graphite Surfaces,
S. Suto, A. Kasuya, S.W. Hu, A. Wawro, T. Goto and Y. Nishina,
Surface Review and Letters 3, (1996) 927-932.

5) Subpicosecond Spectroscopy of the Optical Nonlinearities of CuCl Quantum Dots,
K. Edamatsu, S. Iwai, T. Itoh, S. Yano and T. Goto,
Phys. Rev. B 51 (16), (1995) 11205-11208.

6) Spatial-Confinement Effect on Phonons and Excitons in PbI_2 Microcrystallites,
S. Saito and T. Goto,
Phys. Rev. B 52 (8), (1995) 5929-5934.

7) The Photoluminescence from ZnS/(ZnSe)n/ZnS Single Quantum Well,
S. Koyama, M.Y. Shen, T. Goto, K. Arai, A. Kasuya and T. Yao,
Proc. of the Asia Symposium on Solid State Photophysics, Nara, (1995) 95-98.

8) Subpicosecond Spectroscopy of PbI_2 Microcrystallites Embedded in E-MAA Copolymer,
A. Yamamoto, S. Yano, T. Goto and A. Kasuya
Proc. of the Asia Symposium on Solid State Photophysics, Nara, (1995) 209-212.

9) Diamagnetic Shift of Exciton Level in Ultra-Thin PbI_2 Crystals,
T. Goto, H. Tanaka, M.Y. Shen, S. Sasaki and N. Miura,
Solid State Commun., 97 (7), (1996) 587-590.

10) Non-Radiative Relaxation of Photochromic Fulgide,
J. Takeda, S. Kurita, Y. Yokoyama and T. Goto,
J. Phys. Soc. Jpn. 64 (9), (1995) 3522-3528.

11) Breakdown of the k Selection Rule and the ^1L_b Exciton Bandwidth in Pyrene Microcrystallites,
Y. Oeda, O. Nishi, Y. Matsushima, K. Mizuno, A.H. Matsui, M. Takeshima and T. Goto,
Proc. of the Asia Symposium on Solid State Photophysics, Nara, (1995) 201-204.

12) Exciton Dynamics and Relaxation Process in Permethylsilane,
H. Suzuki, S. Suto, T. Goto, A. Watanabe and M. Matsuda,
Proc. of the Asia Symposium on Solid State Photophysics, Nara, (1995) 99-102.

13) Exciton Dynamics of Poly(methylphenylsilane),
S. Suto, H. Suzuki, T. Goto, A. Watanabe and M. Matsuda,
Proc. of the Asia Symposium on Solid State Photophysics, Nara, (1995) 213-216.

14) Resonant Hyper-Scattering of Orthoexciton in Cu_2O,
M.Y. Shen, S. Koyama, M. Saito, T. Goto and N. Kuroda,
Proc. of the Asia Symposium on Solid State Photophysics, Nara, (1995) 217-220.

Master Theses (March 1996)

M1) Magneto-Optical Effect and Femto Second Dynamics in Excitons of MoS_2.
Y. Kato.

M2) Exciton Dynamics of Polysilane and Origosilane.
H. Suzuki.